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(19) (CA) **CANADIAN PATENT** (12)

(54) **Herbicidal Substituted 1-(2-Halophenyl) Pyrazoles**

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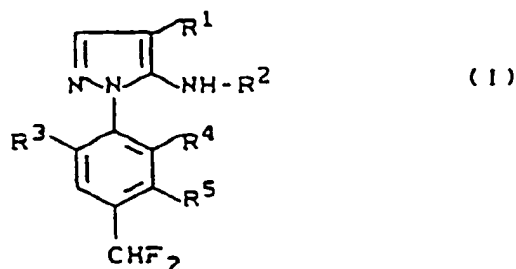
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1-Arylpyrazoles

Abstract

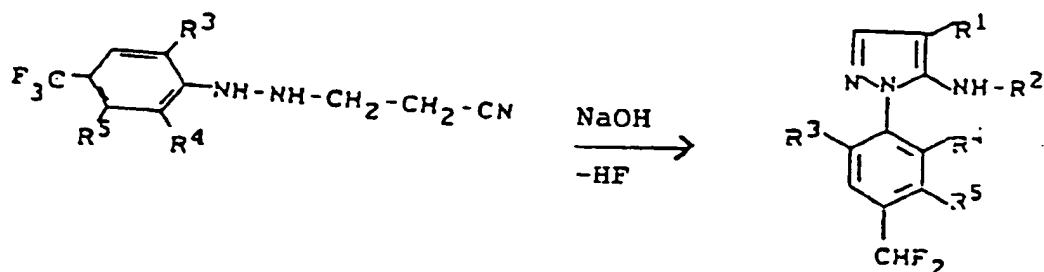
Herbicidal 1-arylpyrazoles of the formula



in which

- R^1 stands for hydrogen or nitro,
 R^2 stands for hydrogen or for a radical $-\overset{\overset{O}{\parallel}}{C}-R^6$,
 R^3 stands for hydrogen or halogen,
 R^4 stands for halogen, and
 R^5 stands for hydrogen or halogen, where
 R^6 stands for haloalkyl, alkoxyalkyl or alkoxyalkoxyalkyl.

Also new are the following process steps:



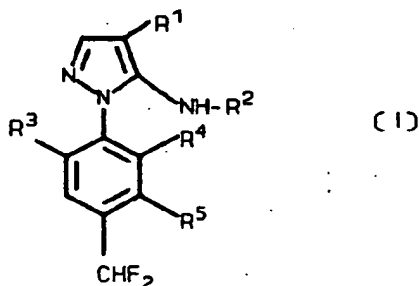
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The invention relates to new 1-arylpyrazoles, several processes to their preparation, and to their use as herbicides.

It is already known that certain 1-arylpyrazoles, such as, for example, 5-amino-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-nitropyrazole, have herbicidal properties (cf., for example, EP 154,115).

The herbicidal activity of these previously known compounds against problem weeds and their tolerance by important crop plants are, however, not entirely satisfactory in all fields of application.

According to one aspect of the present invention there is provided a 1-arylpyrazole of the formula I



in which

R^1 stands for hydrogen or nitro,

R^2 stands for hydrogen or for a radical $-\overset{\overset{O}{\parallel}}{C}-R^6$,

R^3 stands for hydrogen or halogen,

R^4 stands for halogen, and

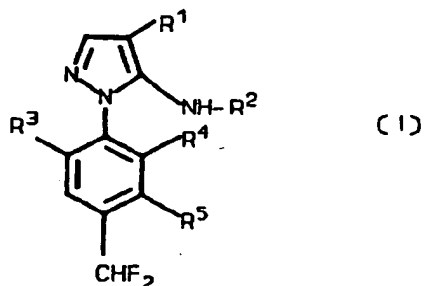
R^5 stands for hydrogen or halogen, where

R^6 stands for alkoxyalkyl or alkoxyalkoxyalkyl, each straight-chain or branched and each having 1 to 6 carbon atoms



in the individual alkyl or alkoxy moieties, or for straight-chain or branched haloalkyl having 1 to 6 carbon atoms and 1 to 9 identical or different halogen atoms.

Furthermore, it has been found that the new 1-aryl-pyrazoles of the general formula (I)

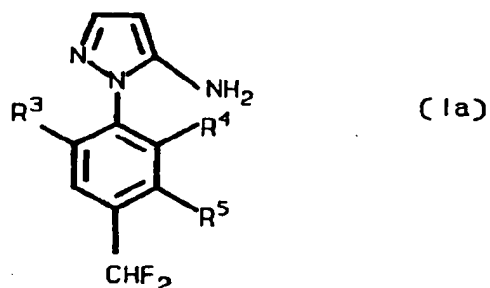


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in which

R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are as defined above are obtained by one of the processes described below:

(a) 1-arylpyrazoles of the formula (Ia)



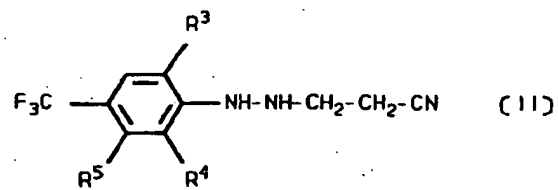
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in which

R^3 , R^4 and R^5 have the abovementioned meaning, are obtained when N-aryl-N'-cyanoethylhydrazines of the formula (II)

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2a



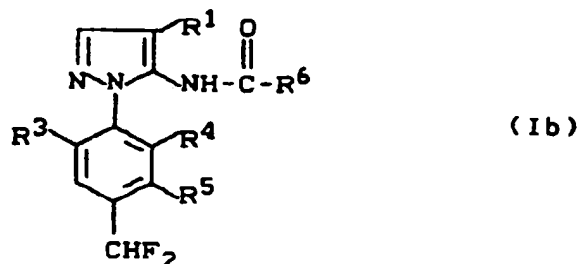
in which

R^3 , R^4 and R^5 have the abovementioned meaning,

B

are cyclized using sodium hydroxide in the presence of a diluent;

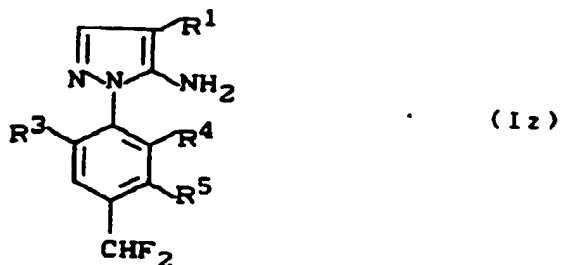
(b) 1-arylpyrazoles of the formula (Ib)



5 in which

R^1 , R^3 , R^4 , R^5 and R^6 have the abovementioned meaning,

are obtained when the 1-arylpyrazoles of the formula (Iz)



10 in which

R^1 , R^3 , R^4 and R^5 have the abovementioned meaning, which can be obtained with the aid of process (a) or (c) according to the invention, are reacted with acylating agents of the formula (III)

15



in which

R^6 has the abovementioned meaning and

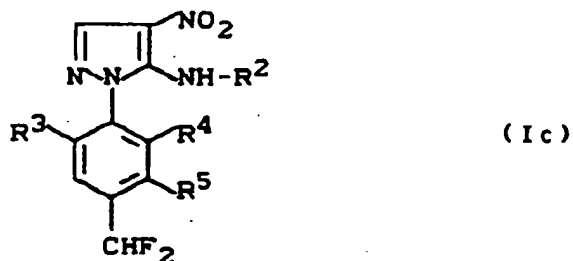
A stands for an electron-withdrawing leaving group,

20 if appropriate in the presence of a diluent and if appropriate in the presence of an acid-binding agent;

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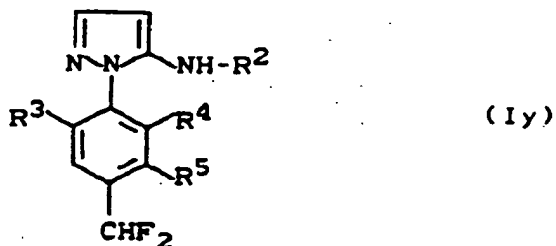
(c) 1-arylpyrazoles of the formula (Ic)



in which

R^2 , R^3 , R^4 and R^5 have the abovementioned meaning,

are obtained when the 1-arylpyrazoles of the formula (Iy)



in which

R^2 , R^3 , R^4 and R^5 have the abovementioned meaning,

which can be obtained with the aid of the process (a) or (b) according to the invention, are reacted with a nitrating agent, if appropriate in the presence of a diluent and if appropriate in the presence of a reaction auxiliary.

Finally, it has been found that the new 1-arylpyrazoles of the general formula (I) have good herbicidal properties, especially also selectively herbicidal properties.

Surprisingly, the 1-arylpyrazoles according to the invention show a considerably improved selectivity towards crop plants in comparison with the 1-arylpyrazoles known from the prior art, such as, for example, 5-amino-4-nitro-1-(2,6-dichloro-4-trifluoromethylphenyl)-pyrazole, which are chemically similar and have a similar

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action, while having a comparably good herbicidal action against problem weeds.

Formula (I) provides a general definition of the 1-arylpyrazoles according to the invention. Preferred compounds of the formula (I) are those in which

R^1 stands for hydrogen or nitro,

R^2 stands for hydrogen or a radical -C-R^6 ,
 \parallel
 O

10

bromine,

R^4 stands for fluorine, chlorine or bromine, and

R^5 stands for hydrogen, fluorine, chlorine or

bromine, where

R^6 , as mentioned above, stands for alkoxyalkyl or alkoxyalkoxy-alkyl, each straight-chain or branched and each having 1 to 6 carbon atoms in the individual alkyl or alkoxy moieties, or for straight-chain or branched haloalkyl having 1 to 6 carbon atoms and 1 to 9 identical or different halogen atoms, especially fluorine, chlorine or bromine. Particularly preferred compounds of the

20

formula (I) are those in which

R^1 stands for hydrogen or nitro,

R^2 stands for hydrogen or for a radical -C-R^6 ,
 \parallel
 O

R^3 stands for hydrogen, fluorine or chlorine,

R^4 stands for fluorine or chlorine, and

R^5 stands for hydrogen, fluorine or chlorine,

where

R^6 stands for methoxymethyl, ethoxymethyl, n- or i-propoxymethyl, methoxyethyl, ethoxyethyl, n- or i-propoxyethyl, methoxyethoxyethyl, ethoxyethoxyethyl, n- or i-propoxyethoxyethyl, trifluoromethyl, trichloromethyl, difluorochloromethyl, difluorochloromethyl, chloromethyl, iodomethyl, bromomethyl, dichloromethyl, 1-chloroethyl, 2-chloroethyl, 2-bromoethyl, 3-chloro-propyl, pentafluoroethyl or heptafluoropropyl.

10

Very particularly preferred compounds of the formula (I) are those in which

R^1 stands for nitro,

R^2 stands for hydrogen or for a radical -C-R^6 ,
 ||
 O

R^3 stands for hydrogen, fluorine or chlorine,

R^4 stands for fluorine or chlorine, and

R^5 stands for hydrogen, fluorine or chlorine,

where

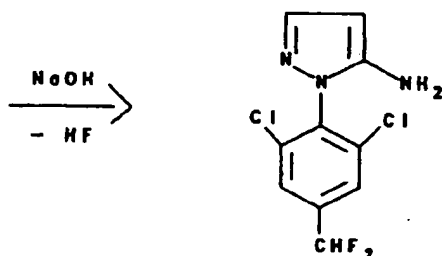
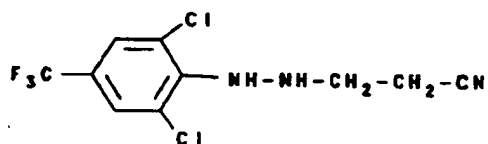
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R^6 stands for methoxymethyl, ethoxymethyl, methoxyethyl, ethoxyethyl, methoxyethoxymethyl, ethoxyethoxyethyl, trifluoromethyl, chloromethyl, dichloromethyl, 1-chloroethyl, 2-chloroethyl, pentafluoroethyl or heptafluoropropyl.

If, for example, N-(2,6-dichloro-4-difluoromethylphenyl)-N'-(2-cyanoethyl-hydrazine is used as the starting compound, the course of the reaction of process

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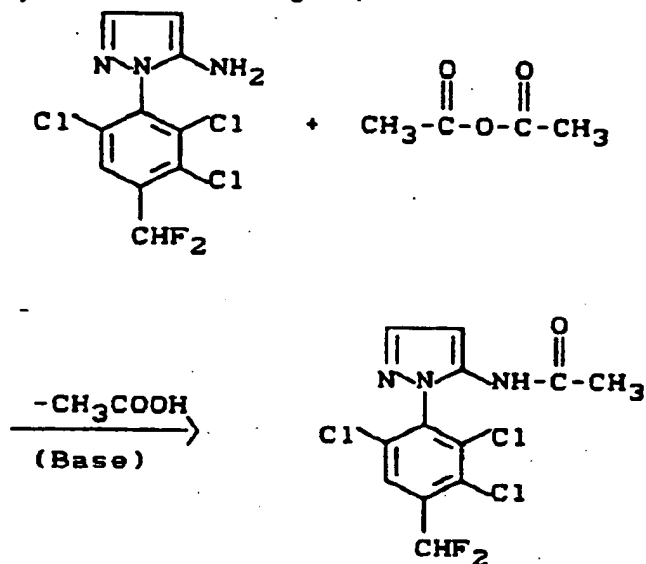
(a) according to the invention may be represented by the following equation:



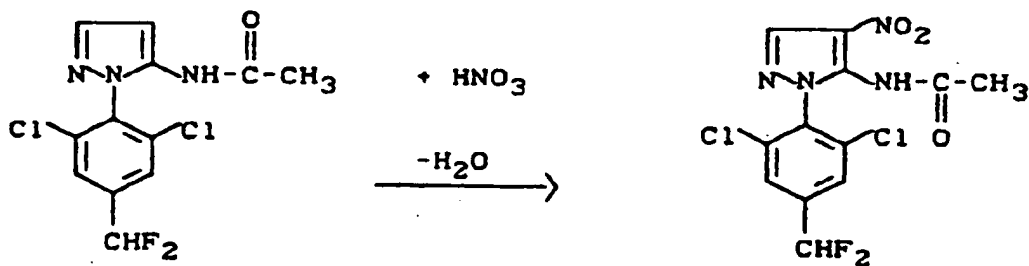
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If, for example, 5-amino-1-(2,3,6-trichloro-4-difluoromethylphenyl)-pyrazole and acetic anhydride are used as the starting compounds, the course of the reac-

tion of process (b) according to the invention may be represented by the following equation:



- 5 If, for example, 5-acetamido-1-(2,6-dichloro-4-difluoromethylphenyl)-pyrazole is used as the starting compound, the course of the reaction of process (c) according to the invention may be represented by the following equation:



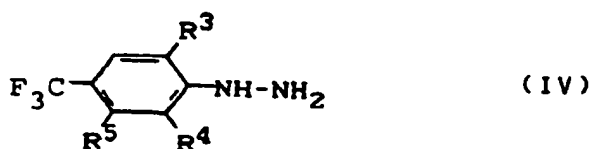
- 10 Formula (II) provides a general definition of the N-aryl-N'-cyanoethyl-hydrazines which are required as starting compounds for carrying out process (a) according to the invention. In this formula (II), R³, R⁴ and R⁵ preferably or particularly preferably stand for those radicals
- 15 which have already been mentioned in connection with the description of the substances of the formula (I) according to the invention as being preferred or particularly

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preferred respectively for these substituents.

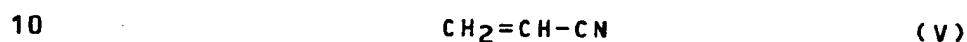
The N-aryl-N'-cyanoethylhydrazines of the formula (II) were hitherto unknown.

They are obtained when 1-arylhidrazines of the
5 formula (IV)



in which

R^3 , R^4 and R^5 have the abovementioned meaning,
are reacted with acrylonitrile of the formula (V)



if appropriate in the presence of a diluent, such as, for example, ethanol, at temperatures between 50°C and 150°C.

The arylhydrazines of the formula (IV) are known or can be obtained in analogy to known processes (cf.,
15 for example, DE-OS (German Published Specification) 3,226,513, DE-OS (German Published Specification) 3,226,496 or EP 224,831).

Acrylonitrile of the formula (V) is a generally known compound of organic chemistry.

20 Formula (Iz) provides a general definition of the 1-arylpyrazoles which are required as starting compounds for carrying out process (b) according to the invention. In this formula (Iz), R^1 , R^3 , R^4 and R^5 preferably stand for those radicals which have already been
25 mentioned in connection with the substances of the formula (I) according to the invention as being preferred for these substituents.

The 1-arylpyrazoles of the formula (Iz) are compounds according to the invention and can be obtained with
30 the aid of process (a) or (c) according to the invention.

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Formula (III) provides a general definition of the acylating agents which are also required as starting compounds for carrying out process (b) according to the invention. In this formula (III), R^6 preferably stands for those radicals which have already been mentioned in connection with the description of the substances of the formula (I) according to the invention as being preferred for this substituent.

A preferably stands for halogen, especially for chlorine or bromine, or for a radical $R^6-\overset{\overset{O}{\parallel}}{C}-O-$,

where

R^6 has the abovementioned meaning.

The acylating agents of the formula (III) are generally known compounds of organic chemistry.

Formula (Iy) provides a general definition of the 1-arylpyrazoles which are required as starting compounds for carrying out process (c) according to the invention. In this formula (Iy), R^2 , R^3 , R^4 and R^5 preferably stand for those radicals which have already been mentioned in connection with the description of the substances of the formula (I) according to the invention as being preferred for these substituents.

The 1-arylpyrazoles of the formula (Iy) are compounds according to the invention and can be obtained with the aid of process (a) or (b) according to the invention.

Suitable diluents for carrying out process (a) according to the invention are customary organic solvents. Alcohols, such as, for example, methanol, ethanol or propanol, or mixtures thereof with water, are preferably used.

When carrying out process (a) according to the invention, the reaction temperatures may be varied within a relatively wide range. In general, the reaction is carried out at temperatures between 30°C and 150°C, preferably at temperatures between 50°C and 120°C.

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For carrying out process (a) according to the invention, 1.0 to 5.0 mol, preferably 1.5 to 3.0 mol, of sodium hydroxide are generally employed per mol of N-aryl-N'-cyanoethylhydrazine of the formula (II). In a suitable diluent, the reaction components are heated for several hours at the reaction temperature necessary, and the reaction is monitored by means of thin-layer chromatography. Working-up and isolation of the reaction products of the formula (Ia) is carried out by generally customary methods.

Suitable diluents for carrying out process (b) according to the invention are inert organic solvents. These include, in particular, aliphatic, alicyclic or aromatic, optionally halogenated hydrocarbons, such as, for example, benzene, toluene, xylene, chlorobenzene, petroleum ether, hexane, cyclohexane, dichloromethane, chloroform or carbon tetrachloride, ethers, such as diethyl ether, dioxane, tetrahydrofuran, ethylene glycol dimethyl ether or ethylene glycol diethyl ether, ketones, such as acetone or butanone, nitriles, such as acetonitrile or propionitrile, amides, such as dimethylformamide, dimethylacetamide, N-methylformanilide, N-methylpyrrolidone or hexamethylphosphoric triamide, esters, such as ethyl acetate, or sulphoxides, such as dimethyl sulphoxide.

If appropriate, process (b) according to the invention is carried out in the presence of a suitable acid-binding agent. Suitable as such are all customary inorganic or organic bases. These include, for example, alkali metal hydroxides, such as sodium hydroxide or potassium hydroxide, alkali metal carbonates, such as sodium carbonate, potassium carbonate or sodium bicarbonate, and also tertiary amines, such as triethylamine, N,N-dimethylaniline, pyridine, N,N-dimethylaminopyridine, diazabicyclooctane (DABCO), diazabicyclononene (DBN) or diazabicycloundecene (DBU).

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When carrying out process (b) according to the invention, the reaction temperatures may be varied within a relatively wide range. In general, the reaction is carried out at temperatures between -20°C and 120°C ,
5 preferably at temperatures between 0°C and 80°C .

For carrying out process (b) according to the invention, 1.0 to 3.0 mol, preferably 1.0 to 1.5 mol, of acylating agent of the formula (III) and, where appropriate, 1.0 to 3.0 mol, preferably 1.0 to 1.5 mol, of
10 acid-binding agent are generally employed per mol of 1-arylpyrazole of the formula (Iz). The reaction is carried out and the reaction products are worked up and isolated by generally customary methods.

Suitable nitrating agents for carrying out process (c) according to the invention are all customary
15 nitrating agents. Concentrated nitric acid or nitrating acid is preferably used.

Suitable diluents for carrying out process (c) according to the invention are all solvents which can conventionally be used for electrophilic substitutions of this
20 type. The acids or mixtures, such as, for example nitric acid or nitrating acid, which are suitable reactants are preferably used simultaneously as diluent. If appropriate, inert organic solvents, such as, for example,
25 glacial acetic acid or chlorinated hydrocarbons, such as methylene chloride, chloroform or carbon tetrachloride, are also suitable diluents.

Suitable catalysts or reaction auxiliaries for carrying out process (c) according to the invention are
30 likewise catalysts which are customary for reactions of this type; acid catalysts, such as, for example, sulphuric acid, iron-III chloride or other Lewis acids, or acetic anhydride, are preferably used.

When carrying out process (c) according to the invention, the reaction temperatures may be varied within
35 a relatively wide range. In general, the reactions are

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carried out between -50°C and $+200^{\circ}\text{C}$, preferably between -20°C and $+150^{\circ}\text{C}$.

For carrying out process (c) according to the invention, 1.0 to 10.0 mol, preferably 1.0 to 5.0 mol, of
5 nitrating agent and, where appropriate, 0.1 to 10 mol of catalyst or reaction auxiliary are generally employed per mol of 1-aryl-pyrazole of the formula (Iy). The reaction is carried out and the reaction products of the formula (Ic) are worked up and isolated in a generally customary
10 manner. Depending on the acid concentration, type of diluent chosen, reaction temperature and duration of the reaction, any acyl groups which may be present on the amino substituent in the 5-position of the pyrazole ring may either be retained or eliminated, in the course of the
15 nitration reaction (in this context, see also the preparation examples).

The active compounds according to the invention can be used as defoliants, desiccants, agents for destroying broad-leaved plants and, especially, as weed-
20 killers. By weeds, in the broadest sense, there are to be understood all plants which grow in locations where they are undesired. Whether the substances according to the invention act as total or selective herbicides depends essentially on the amount used.

25 The active compounds according to the invention can be used, for example, in connection with the following plants:

Dicotyledon weeds of the genera: Sinapis, Lepidium, Galium, Stellaria, Matricaria, Anthemis, Galinsoga, Chenopodium, Urtica, Senecio, Amaranthus, Portulaca, Xanthium,
30 Convolvulus, Ipomoea, Polygonum, Sesbania, Ambrosia, Cirsium, Carduus, Sonchus, Solanum, Rorippa, Rotala, Lindernia, Lamium, Veronica, Abutilon, Emex, Datura, Viola, Galeopsis, Papaver and Centaurea.

35 Dicotyledon cultures of the genera: Gossypium, Glycine, Beta, Daucus, Phaseolus, Pisum, Solanum, Linum, Ipomoea,
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Vicia, Nicotiana, Lycopersicon, Arachis, Brassica, Lactuca, Cucumis and Cucurbita.

Monocotyledon weeds of the genera: Echinochloa, Setaria, Panicum, Digitaria, Phleum, Poa, Festuca, Eleusine, Brachiaria, Lolium, Bromus, Avena, Cyperus, Sorghum, Agropyron, Cynodon, Monochoria, Fimbristylis, Sagittaria, Eleocharis, Scirpus, Paspalum, Ischaemum, Sphenoclea, Dactyloctenium, Agrostis, Alopecurus and Apera.

Monocotyledon cultures of the genera: Oryza, Zea, Triticum, Hordeum, Avena, Secale, Sorghum, Panicum, Saccharum, Ananas, Asparagus and Allium.

However, the use of the active compounds according to the invention is in no way restricted to these genera, but also extends in the same manner to other plants.

The compounds are suitable, depending on the concentration, for the total combating of weeds, for example on industrial terrain and rail tracks, and on paths and squares with or without tree plantings. Equally, the compounds can be employed for combating weeds in perennial cultures, for example afforestations, decorative tree plantings, orchards, vineyards, citrus groves, nut orchards, banana plantations, coffee plantations, tea plantations, rubber plantations, oil palm plantations, cocoa plantations, soft fruit plantings and hopfields, and for the selective combating of weeds in annual cultures.

The active compounds according to the invention can be employed with particularly good success for the selective combating of dicotyledon weeds in monocotyledon and dicotyledon cultures, such as, for example, wheat, maize, rice or soybean.

At suitable application rates, the active compounds according to the invention furthermore have a plant growth-regulating action, and can be employed, for example, as defoliants.

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The active compounds can be converted into the customary formulations, such as solutions, emulsions, wettable powders, suspensions, powders, dusting agents, pastes, soluble powders, granules, suspension-emulsion
5 concentrates, natural and synthetic materials impregnated with active compound, and very fine capsules in polymeric substances.

These formulations are produced in known manner, for example by mixing the active compounds with extenders,
10 that is liquid solvents and/or solid carriers, optionally with the use of surface-active agents, that is emulsifying agents and/or dispersing agents and/or foam-forming agents.

In the case of the use of water as an extender,
15 organic solvents can, for example, also be used as auxiliary solvents. As liquid solvents, there are suitable in the main: aromatics, such as xylene, toluene or alkyl-naphthalenes, chlorinated aromatics and chlorinated aliphatic hydrocarbons, such as chlorobenzenes, chloroethy-
20 enes or methylene chloride, aliphatic hydrocarbons, such as cyclohexane or paraffins, for example petroleum fractions, mineral and vegetable oils, alcohols, such as butanol or glycol as well as their ethers and esters, ketones, such as acetone, methyl ethyl ketone, methyl
25 isobutyl ketone or cyclohexanone, strongly polar solvents, such as dimethylformamide and dimethyl sulphoxide, as well as water.

As solid carriers there are suitable: for example ammonium salts and ground natural minerals, such as kao-
30 lins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals, such as highly disperse silicic acid, alumina and silicates, as solid carriers for granules there are suitable: for example crushed and fractionated natural rocks
35 such as calcite, marble, pumice, sepiolite and dolomite, as well as synthetic granules of inorganic and organic

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meals, and granules of organic material such as sawdust, coconut shells, maize cobs and tobacco stalks; as emulsifying and/or foam-forming agents there are suitable: for example non-ionic and anionic emulsifiers, such as polyoxyethylene-fatty acid esters, polyoxyethylene-fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkylsulphonates, alkylsulphates, arylsulphonates as well as albumin hydrolysis products; as dispersing agents there are suitable: for example lignin-sulphite waste liquors and methylcellulose.

Adhesives such as carboxymethylcellulose and natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, as well as natural phospholipids, such as cephalins and lecithins, and synthetic phospholipids, can be used in the formulations. Further additives can be mineral and vegetable oils.

It is possible to use colorants such as inorganic pigments, for example iron oxide, titanium oxide and Prussian Blue, and organic dyestuffs, such as alizarin dyestuffs, azo dyestuffs and metal phthalocyanine dyestuffs, and trace nutrients such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

The formulations in general contain between 0.1 and 95 per cent by weight of active compound, preferably between 0.5 and 90%.

The active compounds according to the invention, as such or in the form of their formulations, can also be used, for combating weeds, as mixtures with known herbicides, finished formulations or tank mixes being possible.

Suitable components for the mixtures are known herbicides, such as, for example, 1-amino-6-ethylthio-3-(2,2-di-methylpropyl)-1,3,5-triazine-2,4(1H,3H)-dione or N-(2-benzthiazolyl)-N,N'-dimethylurea for combating weeds in cereals; 4-amino-3-methyl-6-phenyl-1,2,4-

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- triazin-5(4H)-one for combating weeds in sugar beet, and 4-amino-6-(1,1-dimethylethyl)-3-methylthio-1,2,4-triazin-5(4H)-one for combating weeds in soybeans. Where appropriate, mixtures with 2,4-dichlorophenoxyacetic acid;
- 5 2,4-dichlorophenoxypropionic acid; 4-(2,4-dichlorophenoxy)-butyric acid; (2-methyl-4-chlorophenoxy)-acetic acid; (4-chloro-2-methylphenoxy)-propionic acid; 3,5,6-trichloro-2-pyridyloxyacetic acid; 2-[4-(2,4-dichlorophenoxy)-phenoxy]-propionic acid, its methyl ester or its ethyl ester;
- 10 2-[4-[(6-chloro-2-benzoxazolyl)-oxy]-phenoxy]-propanoic acid, its methyl ester or its ethyl ester; butyl 2-[4-(5-trifluoromethyl-2-pyridinyloxy)-phenoxy]-propanoate; trimethylsilylmethyl 2-[4-(3,5-dichloropyrid-2-yloxy)-phenoxy]-propionate; 2-[4-[(3-chloro-5-(trifluoromethyl)-2-pyridinyl)-oxy]-phenoxy]-propanoic acid, or ethyl 2-[4-[(3-chloro-5-(trifluoromethyl)-2-pyridinyl)-oxy]-phenoxy]-propanoate; 3,6-dichloro-2-pyridinecarboxylic acid; 2,6-diethyl-N-(methoxymethyl)chloroacetanilide; N-(butoxy-methyl)-2-chloro-N-(2,6-diethylphenyl)-acetamide; 2-
- 20 chloro-N-(2,6-dimethylphenyl)-N-[(1H)-pyrazol-1-yl-methyl]-acetamide; 2-ethyl-6-methyl-N-(1-methyl-2-methoxyethyl)-chloroacetanilide; α -chloro-2',6'-diethyl-N-(2-propoxyethyl)-acetanilide; 2-chloro-N-isopropylacetanilide; 4-(di-n-propylamino)-3,5-dinitrobenzenesulphonamide; N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitroaniline;
- 25 2,6-dinitro-4-trifluoromethyl-N,N-dipropylaniline; 5-(2-chloro-4-trifluoromethyl-phenoxy)-2-nitrobenzoic acid; methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate; 5-(2-chloro-4-trifluoromethyl-phenoxy)-N-methylsulphonyl-2-
- 30 nitrobenzamide; 2-ethoxy-1-methyl-2-oxo-ethyl 5-[2-chloro-4-(trifluoromethyl)-phenoxy]-2-nitrobenzoate; N,N-dimethyl-N'-(3-chloro-4-methylphenyl)-urea; N,N-dimethyl-N'-(4-isopropylphenyl)-urea; 2-[1-(ethoximino)-butyl]-3-hydroxy-5-[tetrahydro-(2H)-thiopyran-3-yl]-2-
- 35 cyclohexen-1-one; 2-[1-(ethoxamino)-butylidene]-5-(2-ethylthiopropyl)-1,3-cyclohexadione; 2-[4,5-dihydro-4-
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methyl-4-isopropyl-5-oxo-(1H)-imidazol-2-yl]-5-ethyl-
 pyridine-3-carboxylic acid; methyl 2-[4,5-dihydro-4-
 methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-4(5)-
 methylbenzoate; 2-[5-methyl-5-(1-methylethyl)-4-oxo-2-
 5 imidazolin-2-yl]-3-quinolinecarboxylic acid; 3,5-dibromo-
 4-hydroxy-benzonitrile; 3,5-diiodo-4-hydroxybenzonitrile;
 N-methyl-2-(1,3-benzothiazol-2-yloxy)-acetanilide;
 methyl 2-[[[[[(4,6-dimethoxypyrimidin-2-yl)-amino]-
 carbonyl]-amino]-sulphonyl]-methyl]-benzoate; ethyl 2-
 10 [[[(4-chloro-6-methoxy-2-pyrimidinyl)-aminocarbonyl]-
 aminosulphonyl]-benzoate; 2-chloro-N-[[[(4-methoxy-6-
 methyl-1,3,5-triazin-2-yl)-amino]-carbonyl]-benzene-
 sulphonamide; 2-[[[(4-methoxy-6-methyl-1,3,5-triazin-
 2-yl)-amino]-carbonyl]-amino]-sulphonyl]-benzoic acid or
 15 its methyl ester; methyl 2-[[[(4,6-dimethyl-2-pyrimidinyl)-
 aminocarbonyl]-aminosulphonyl]-benzoate; methyl 3-[[[[[(4-
 methoxy-6-methyl-1,3,5-triazin-2-yl)-amino]-carbonyl]-
 amino]-sulphonyl]-thiophene-2-carboxylate; S-ethyl N,N-
 di-n-propyl-thiocarbamate; S-ethyl N,N-hexamethylene-
 20 thiolcarbamate; S-[(4-chlorophenyl)-methyl] N,N-diethyl-
 thiocarbamate; S-(2,3,3-trichloroallyl) N,N-diisopropyl-
 thiolcarbamate; 2-chloro-4-ethylamino-6-isopropylamino-
 1,3,5-triazine; 2-chloro-4-ethylamino-6-(3-cyanopropyl-
 amino)-1,3,5-triazine; 2,4-bis-[N-ethyl-amino]-6-methyl-
 25 thio-1,3,5-triazine; 4-ethylamino-2-t-butylamino-6-
 methylthio-s-triazine; 4-amino-6-t-butyl-3-ethylthio-
 1,2,4-triazin-5(4H)-one; 3-isopropyl-2,1,3-benzothia-
 diazin-4-one 2,2-dioxide; exo-1-methyl-4-(1-methylethyl)-
 2-(2-methylphenyl-methoxy)-7-oxabicyclo-(2,2,1)-heptane
 30 and 0-(6-chloro-3-phenyl-pyridazin-4-yl) S-octyl thio-
 carbonate are advantageous.

Some mixtures surprisingly also exhibit a synergistic effect.

Mixtures with other known active compounds, such
 35 as fungicides, insecticides, acaricides, nematocides, bird
 repellants, plant nutrients and agents which improve soil
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structure, are also possible.

The active compounds can be used as such, in the form of their formulations or in the use forms prepared therefrom by further dilution, such as ready-to-use solutions, suspensions, emulsions, powders, pastes and granules. They are used in the customary manner, for example by watering, spraying, atomizing or scattering.

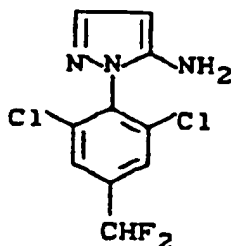
The active compounds according to the invention can be applied either before or after emergence of the plants. They can also be incorporated into the soil before sowing.

The amount of active compound used can vary within a substantial range. It depends essentially on the nature of the desired effect. In general, the amounts used are between 0.01 and 10 kg of active compound per hectare of soil surface, preferably between 0.05 and 5 kg per ha.

The preparation and use of the active compounds according to the invention are evident from the examples which follow.

Preparation Examples

Example 1



(Process a)

29.8 g (0.1 mol) of N-(2,6-dichloro-4-trifluoromethylphenyl)-N'-(2-cyanoethyl)-hydrazine in 200 ml of ethanol are heated at the reflux temperature for 2 hours together with 18 g (0.2 mol) of 45% strength technical grade sodium hydroxide solution. After the reaction has ended (monitor by thin-layer chromatography; dichloromethane/methanol 19 : 1), the mixture is evaporated in

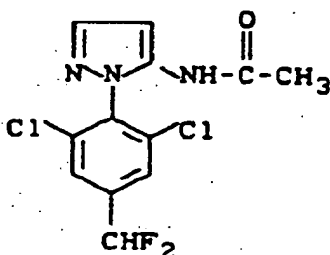
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vacuo, the residue is taken up in dichloromethane/water, the organic phase is separated off, washed with water and dried over sodium sulphate, and the solvent is removed in vacuo. After recrystallization from 500 ml of toluene, 5 16 g (58% of theory) of 5-amino-1-(2,6-dichloro-4-difluoromethylphenyl)-pyrazole of melting point 110°C - 111°C are obtained.

^{19}F -NMR (CDCl_3) : $\delta = 34.3$ (d, 2F) ppm.

Example 2

10

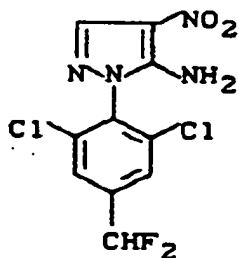


(Process b)

2 ml (0.021 mol) of acetic anhydride are added dropwise to 5.56 g (0.02 mol) of 5-amino-1-(2,6-dichloro-4-difluoromethylphenyl)-pyrazole in 40 ml of toluene at 15 20°C with stirring, the mixture is stirred for a further 16 hours at room temperature after the addition has ended, the precipitate formed is filtered off with suction, and the residue is dried.

5.4 g (84% of theory) of 5-acetamido-1-(2,6-dichloro-4-difluoromethylphenyl)-pyrazole of melting 20 point 209°C - 211°C are obtained.

Example 3



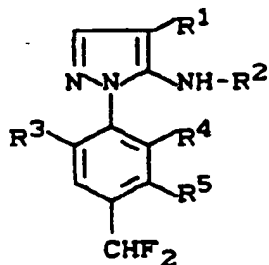
(Process c)

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1.07 ml of 98% strength nitric acid are added drop-wise with stirring to 4.8 g (0.015 mol) of 5-acetamido-1-(2,6-dichloro-4-difluoromethylphenyl)-pyrazole in 40 ml of concentrated sulphuric acid at -20°C , the mixture is stirred for 4
 5 hours at 20°C after the addition has ended, the reaction mixture is poured onto ice, the precipitated solid is filtered off with suction and dissolved in dichloromethane, and the solution is washed once each with water and with aqueous sodium bicarbonate solution and dried over sodium sulphate,
 10 and the solvent is removed in vacuo.

4.0 g (83% of theory) of 5-amino-1-(2,6-dichloro-4-difluoromethylphenyl)-4-nitro-pyrazole of melting point $165^{\circ}\text{C} - 168^{\circ}\text{C}$ are obtained.

The following 1-arylpyrazoles of the general
 15 formula (I)

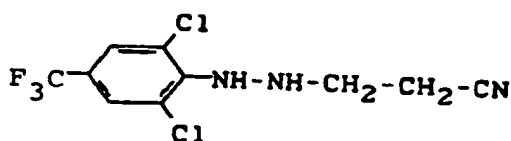


(I)

are obtained in a corresponding manner and according to the general data for the preparation:

Table 1

	Example No.	R ¹	R ²	R ³	R ⁴	R ⁵	Melting point
5	4	H	H	Cl	Cl	Cl	¹ H-NMR*); 5.2; 5.4; 7.25; 7.35; 7.9
10	5	H	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{CHCl}_2 \end{array}$	Cl	Cl	H	91-92
	6	NO ₂	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{CHCl}_2 \end{array}$	Cl	Cl	H	104-106
15	7	NO ₂	$\begin{array}{c} \text{Cl} \\ \\ -\text{CO}-\text{CH}-\text{CH}_3 \end{array}$	Cl	Cl	H	107-113
	8	NO ₂	-CO-CH ₃	Cl	Cl	H	¹ H-NMR*); 8.35
	9	NO ₂	$\begin{array}{c} \text{Cl} \\ \\ -\text{CO}-\text{CH}-\text{C}_2\text{H}_5 \end{array}$	Cl	Cl	H	79-87
20	*) The ¹ H-NMR spectrum was recorded in hexadeutero-dimethyl sulphoxide (DMSO-d ₆) using tetramethylsilane (TMS) as the internal standard. The chemical shift is given as the δ-value in ppm.						

Preparation of the starting compounds25 Example II-1

30

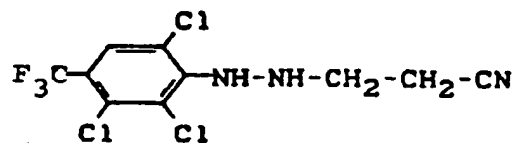
24.5 g (0.1 mol) of 2,6-dichloro-4-trifluoromethyl-phenylhydrazine and 6 g (0.11 mol) of acrylonitrile are heated at the reflux temperature for 4 days in 100 ml of ethanol. After the volatile constituents have been removed in vacuo, 30 g (99% of theory) of N-(2,6-dichloro-4-trifluoromethylphenyl)-N-(2-cyanoethyl)-hydrazine are obtained as an oil.

¹H-NMR (CDCl₃/TMS): δ = 2.55; 3.1; 4.55; 6.0; 7.55 ppm.

In a corresponding manner,

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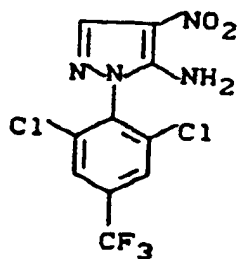
Example II-2:



melting point 47°C - 49°C
is obtained.

5 Use Examples

In the following use examples, the compound shown below was used as the comparison substance:



(A)

5-amino-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-
10 nitropyrazole (known from EP 154,115/ Example No. 50).

Example A

Pre-emergence test

Solvent: 5 parts by weight

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

5 To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent, the stated amount of emulsifier is added and the concentrate is diluted with water to the desired concentration.

10 Seeds of the test plants are sown in normal soil and, after 24 hours, watered with the preparation of the active compound. It is expedient to keep constant the amount of water per unit area. The concentration of the active compound in the preparation is of no importance, only the amount of active compound applied per unit area being decisive. After three weeks, the degree of damage to the plants is rated in % damage in comparison to the development of the untreated control. The figures denote:

20 0% = no action (like untreated control)

100% = total destruction

In this test, a significant superiority in the crop plant selectivity over comparison substance (A) with comparable herbicidal activity is shown in this test by, for example, the compounds of the following Preparation Examples: 3, 6 and 7.

25

Example B

Post emergence test

Solvent: 5 parts by weight of acetone

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

5 To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent, the stated amount of emulsifier is added and the concentrate is diluted with water to the desired concentration.

10 Test plants which have a height of 5 - 15 cm are sprayed with the preparation of the active compound in such a way as to apply the particular amounts of active compound desired per unit area. The concentration of the spray liquor is so chosen that the particular amounts of active
15 compound desired are applied in 2,000 l of water/ha. After three weeks, the degree of damage to the plants is rated in % damage in comparison to the development of the untreated control. The figures denote:

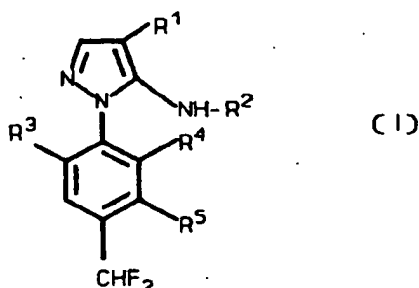
0% = no action (like untreated control)

20 100% = total destruction

In this test, a significant superiority in the crop plant selectivity over comparison substance (A) with comparable herbicidal activity is shown in this test by, for example, the compounds of the following Preparation
25 Examples: 3 and 6.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A 1-arylpyrazole of the formula I



in which

R^1 stands for hydrogen or nitro,

R^2 stands for hydrogen or for a radical $-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-R^6$,

R^3 stands for hydrogen or halogen,

R^4 stands for halogen, and

R^5 stands for hydrogen or halogen, where

R^6 stands for alkoxyalkyl or alkoxyalkoxyalkyl, each straight-chain or branched and each having 1 to 6 carbon atoms in the individual alkyl or alkoxy moieties, or for straight-chain or branched haloalkyl having 1 to 6 carbon atoms and 1 to 9 identical or different halogen atoms.

2. A 1-arylpyrazole according to claim 1,

in which

R^1 stands for hydrogen or nitro,

R^2 stands for hydrogen or a radical $-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-R^6$,

R^3 stands for hydrogen, fluorine, chlorine or bromine,
 R^4 stands for fluorine, chlorine or bromine, and
 R^5 stands for hydrogen, fluorine, chlorine or bromine,
 where

R^6 is as defined in claim 1.

3. A 1-arylpyrazole according to claim 1,
 in which

R^1 stands for hydrogen or nitro,
 R^2 stands for hydrogen or for a radical $-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{R}^6$,

R^3 stands for hydrogen, fluorine or chlorine,
 R^4 stands for fluorine or chlorine, and
 R^5 stands for hydrogen, fluorine or chlorine,

where

R^6 stands for methoxymethyl, ethoxymethyl, n- or i-propoxymethyl, methoxyethyl, ethoxyethyl, n- or i-propoxyethyl, methoxyethoxyethyl, ethoxyethoxyethyl, n- or i-propoxyethoxyethyl, trifluoromethyl, trichloromethyl, dichlorofluoromethyl, difluorochloromethyl, chloromethyl, iodomethyl, bromomethyl, dichloromethyl, 1-chloroethyl, 2-chloroethyl, 2-bromoethyl, 3-chloropropyl, pentafluoroethyl or heptafluoropropyl.

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4. A 1-arylpyrazole according to claim 1,

in which

R^1 stands for nitro,

R^2 stands for hydrogen or for a radical $-\overset{\overset{O}{\parallel}}{C}-R^6$,

R^3 stands for hydrogen, fluorine or chlorine,

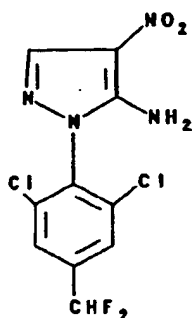
R^4 stands for fluorine or chlorine, and

R^5 stands for hydrogen, fluorine or chlorine,

where

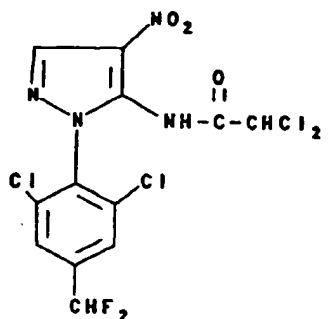
R^6 stands for methoxymethyl, ethoxymethyl, methoxyethyl, ethoxyethyl, methoxyethoxyethyl, ethoxyethoxyethyl, trifluoromethyl, chloromethyl, dichloromethyl, 1-chloroethyl, 2-chloroethyl, pentafluoroethyl or heptafluoropropyl.

5. 5-Amino-1-(2,6-dichloro-4-difluoromethylphenyl)-4-nitro-pyrazole of the formula

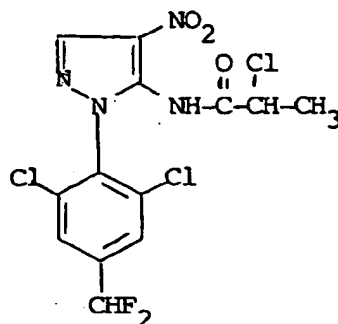


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6. 5-Dichloroacetamido-1-(2,6-dichloro-4-difluoromethyl-phenyl)-4-nitro-pyrazole of the formula



7. 5-(α -Chloropropionamido)-1-(2,6-dichloro-4-difluoromethyl-phenyl)-4-nitro-pyrazole of the formula



8. A herbicidal composition comprising a herbicidally effective amount of a compound according to any one of claims 1 to 7 in admixture with a suitable carrier or diluent.
9. A herbicidal composition comprising a herbicidally effective amount of a compound according to any one of claims 1 to 7 in admixture with a solid diluent or carrier, a liquified normally gaseous diluent or carrier, or a liquid diluent or carrier containing a surface active agent.
10. A method of combating weeds which comprises applying to the weeds, or to a habitat thereof, a herbicidally effective amount of a compound according to any one of claims 1 to 7.
11. A method of combating weeds which comprises applying to the weeds, or to a habitat thereof, a herbicidally effective amount of a composition containing a compound according to any one of claims 1 to 7 in admixture with a suitable carrier or diluent.

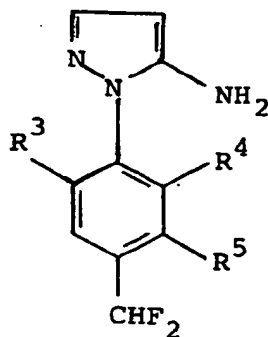
12. A method of combating weeds which comprises applying to the weeds, or to a habitat thereof, a herbicidally effective amount of a composition containing between 0.1 and 95% by weight of a compound according to any one of claims 1 to 7 in admixture with a suitable carrier or diluent.
13. A method of combating weeds which comprises applying to the weeds, or to a habitat thereof, a herbicidally effective amount of a composition containing between 0.5 and 90% by weight of a compound according to any one of claims 1 to 7 in admixture with a suitable carrier or diluent.
14. A method of combating weeds which comprises applying to the weeds, or to a habitat thereof, a herbicidally effective amount of a compound according to any one of claims 1 to 7 wherein the compound is applied as a pre-emergence herbicide.
15. A method of combating weeds which comprises applying to the weeds, or to a habitat thereof, a herbicidally effective amount of a compound according to any one of claims 1 to 7 wherein the compound is applied as a post-emergence herbicide.
16. A method of combating weeds which comprises applying to the weeds, or to a habitat thereof, a herbicidally effective amount of a compound according to any one of claims 1 to 7 wherein the compound is applied to an area of cultivation at a rate of between 0.01 and 10kg/ha.

17. A method of combating weeds which comprises applying to the weeds, or to a habitat thereof, a herbicidally effective amount of a compound according to any one of claims 1 to 7 wherein the compound is applied to an area of cultivation at a rate of between 0.05 and 5kg/ha.

18. A process for preparing a compound according to claim 1, wherein

R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are as defined in claim 1, which process comprises

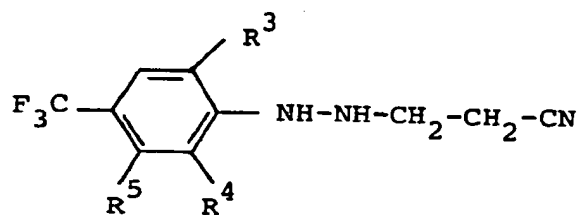
(a) for a 1-arylpyrazole of the formula (Ia)



(Ia)

in which

R^3 , R^4 and R^5 have the abovementioned meaning, cyclizing an N-aryl-N'-cyanoethylhydrazine of the formula (II)

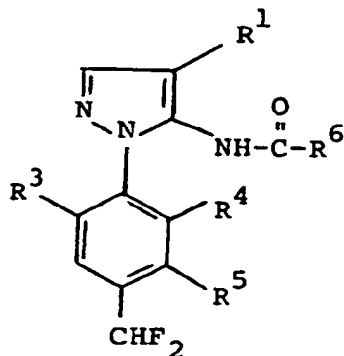


(II)

in which

R^3 , R^4 and R^5 have the abovementioned meaning, with sodium hydroxide in contact with a diluent; or

(b) for a 1-arylpyrazole of the formula (Ib)

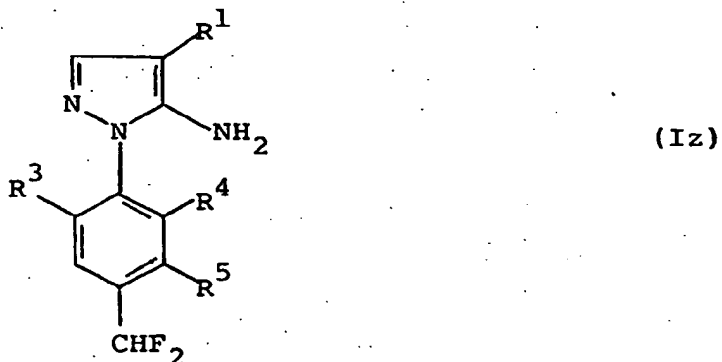


(Ib)

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in which

R^1 , R^3 , R^4 , R^5 and R^6 have the abovementioned meaning,
reacting a 1-arylpirazole of the formula (Iz)



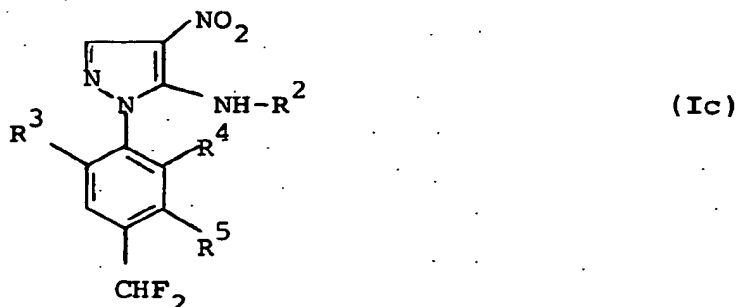
in which

R^1 , R^3 , R^4 and R^5 have the abovementioned meaning,
obtained by process (a) defined above, or (c) defined below, with an
acylating agent of the formula (III)



in which

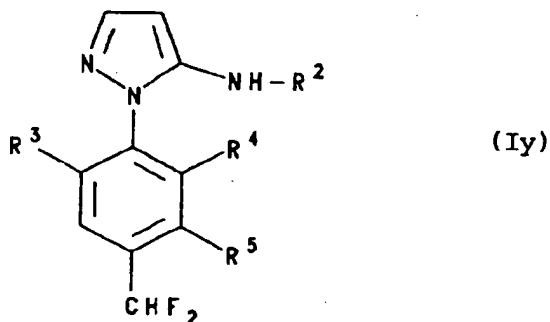
R^6 has the abovementioned meaning, and
A stands for an electron-withdrawing leaving group; or
(c) for a 1-arylpirazole of the formula (Ic)



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in which

R^2 , R^3 , R^4 and R^5 have the abovementioned meaning,
nitrating a 1-arylpyrazole of the formula (Iy)

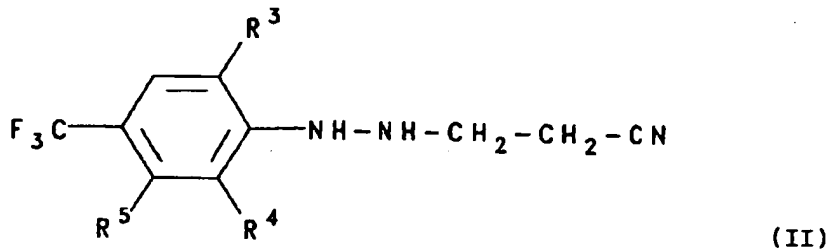


in which

R^2 , R^3 , R^4 and R^5 have the abovementioned meaning,
obtained by process (a) or (b) defined above.

19. A process for preparing a herbicidal composition which comprises mixing a 1-arylpyrazole of the formula (I) according to any one of claims 1 to 7 with a diluent or carrier or a surface active agent.

20. An N-aryl-N'-cyanoethylhydrazine of the formula (II)

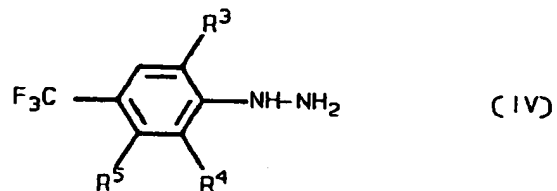


in which

R^3 , R^4 and R^5 are as defined in claim 1.

21. A process for preparing a compound according to claim 20, wherein

R^3 , R^4 and R^5 are as defined in claim 20, which process comprises reacting a 1-arylhydrazine of the formula (IV)



in which

R^3 , R^4 and R^5 have the abovementioned meaning, with acrylonitrile of the formula (V)



at a temperature between 50°C and 150°C .

FETHERSTONHAUGH & CO.
OTTAWA, CANADA

PATENT AGENTS

